COLORADO
DEPARTMENT OF AGRICULTURE

Agricultural Chemicals and Groundwater Protection

Arkansas Valley – 2010 Groundwater Monitoring Report

The Agricultural Chemicals & Groundwater Protection Program is responsible for conducting monitoring to detect the presence of commercial fertilizer constituents and pesticide compounds (agrichemicals) in groundwater throughout Colorado. This program has been established to provide current, scientifically valid, groundwater quality data to the Commissioner of Agriculture and the general public.

This report discusses monitoring history in the Arkansas Valley monitoring well network, sample collection and analysis information for the 2010 field season, as well as statistics and maps detailing laboratory results. Any information pertaining to sampling frequency and purpose, sampling network development, laboratory methodology and protocol, Arkansas Valley location and character, and long–term history of the Program, is available in greater detail from these documents found on the Program webpage (http://www.colorado.gov/ag/gw):

- Agricultural Chemicals & Groundwater Protection 1990–2006
- Program Monitoring Strategy 2007–2017
- Agricultural Chemicals & Groundwater Protection Program Sampling SOP Manual
- Groundwater Quality Database
- Colorado Dept. of Agriculture Groundwater Laboratory Analytical SOPs

Groundwater Quality Monitoring History

The Program began monitoring activities in the Arkansas Valley in 1994 when it was decided that land use and hydrogeologic factors in the study area created the potential for migration of agricultural chemicals into groundwater. A sampling of 139 domestic, stock, and irrigation wells through the valley were analyzed for the presence of nitrate and pesticide compounds, as well as a suite of basic water quality constituents and dissolved metals.

Groundwater in portions of the Arkansas Valley was found to be impacted by nitrate and certain pesticide compounds. Fourteen percent (19 of 139) of wells sampled showed nitrate levels in excess of the United States Environmental Protection Agency's (EPA) drinking water standard of 10.0 milligrams–per–liter (mg L^{-1}) or parts–per–million (ppm). A vast majority of the wells sampled (80%) tested positive for nitrate but were below the EPA standard, and samples from eight wells contained no detectable nitrate above the detection limit of 0.5 ppm. It is common that naturally occurring nitrate–nitrogen can account for up to 2.5 ppm in groundwater samples. The maximum concentration discovered was 39.1 ppm, while the other 18 wells with concentrations over the EPA standard, were less than 20 ppm. Distribution of the wells, exceeding the EPA standard, was found to be concentrated in three areas: Pueblo County near Avondale, Otero County between Fowler and La Junta, and Prowers County near Lamar and Granada.

Of the 30 pesticide compounds screened for, only three were detected in 1994. However, laboratory and data analysis at the time allowed for the reporting of trace detections which are not quantifiable. A detection is designated 'Trace' when there is evidence it exists yet not at a great enough concentration to be above the minimum detection level. Twelve trace detections of atrazine, and one each of metolachlor and 2,4–D were discovered in 1994. The limit of detection for atrazine was 0.5 micrograms–per–liter (µg L^{-1}) or parts–per–billion (ppb).

In 1995, the Program conducted a follow–up sampling of the 32 wells with a pesticide detection or nitrate concentration above the EPA standard in 1994. Ultimately, only 28 of the 32 wells were resampled due to two

wells being out of service and two others inaccessible for sampling. The intent of this 1995 sampling was to determine if the contamination originally detected was representative of the groundwater quality at the respective sites, or only a coincidence of sampling time.

Of the 19 wells that had nitrate in excess of the EPA standard in 1994, four decreased to below the standard. The high mobility of nitrate combined with this hydraulically active groundwater system can produce significant swings in nitrate concentrations from year to year, but overall, the differences between the 1994 and 1995 samplings were not statistically significant. Of the wells that were resampled due to previous pesticide detection, the 1995 sampling showed four wells previously with trace detections of atrazine, falling below the 1995 detection limit of 0.1 ppb. Seven other wells contained atrazine with concentrations ranging from 0.12 to 4.20 ppb. The one well at 4.20 ppb, exceeded the EPA drinking water standard of 3.0 ppb after only showing a trace level in 1994. The wells with metolachlor and 2,4–D trace detections were both below the detection limits for those compounds in 1995.

In 2004, the Program installed a network of 20 permanent, dedicated monitoring wells into the alluvial aquifer of the Arkansas River extending eastward from the eastern edge of Pueblo to the town of Holly. Placement of the wells was based on previous monitoring data from the 1994 and 1995 sampling events, agricultural chemical use data, and aquifer sensitivity/vulnerability models developed by the Program in 1996. The network was first sampled in 2004, shortly after installation, and has also been sampled in 2005 and 2008. The Program has since given the Arkansas Valley network a sampling priority of once every two years.

Sampling of the monitoring well network, in general, has shown very few instances of significant groundwater quality impact from agricultural chemicals. Initial sampling in 2004 of 19 of the 20 monitoring wells (one was damaged and in need of repair) showed only one well with nitrate in excess of the EPA standard and 17 wells ranging from less than 10.0 ppm to the 0.1 ppm detection limit. Twelve of the 18 wells with detectable nitrate were less than five ppm. The one sampling point exceeding the EPA standard was located between Fowler and La Junta which is one of main areas discovered to have elevated nitrate levels after sampling in 1994 and 1995.

Pesticide results from 2004 revealed just four pesticide compounds being detected: atrazine, metolachlor, 2,4–D, and desethyl atrazine (DEA). One well had a detection of both atrazine and DEA and the three other detections were of metolachlor, atrazine, and 2,4–D in separate wells. Concentrations were minimal with the highest being a 0.58 ppb detection of metolachlor. A resample of the network in 2005, including the repaired well not sampled in 2004, confirmed much of what was discovered in 2004. Only one well contained nitrate above the EPA standard, and three wells were below the detection limit of 0.1 ppm. The median nitrate concentration was just over two ppm. A detection of metolachlor at 0.059 ppb and a detection of DEA at 0.079 ppb were the only pesticides discovered in 2005. Both detections were discovered in the same wells of initial discovery in 2004, and concentrations decreased by more than 50% in both wells.

In 2008, 19 of 20 wells were sampled (another well near Lamar was damaged) and the median nitrate increased to 4.1 ppm with four wells containing nitrate in excess of the EPA standard. Pesticide results for 2008

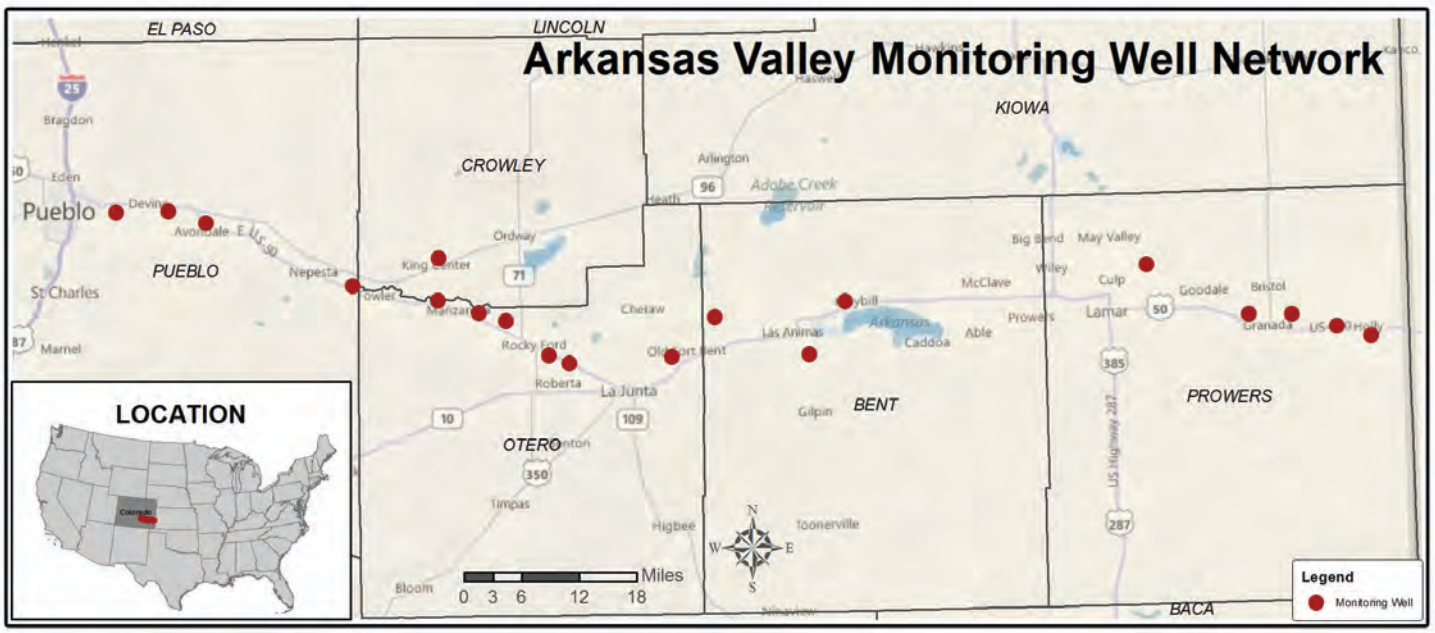

Figure 1. Locations of monitoring wells in the Arkansas Valley Monitoring Well Network as of 2010.

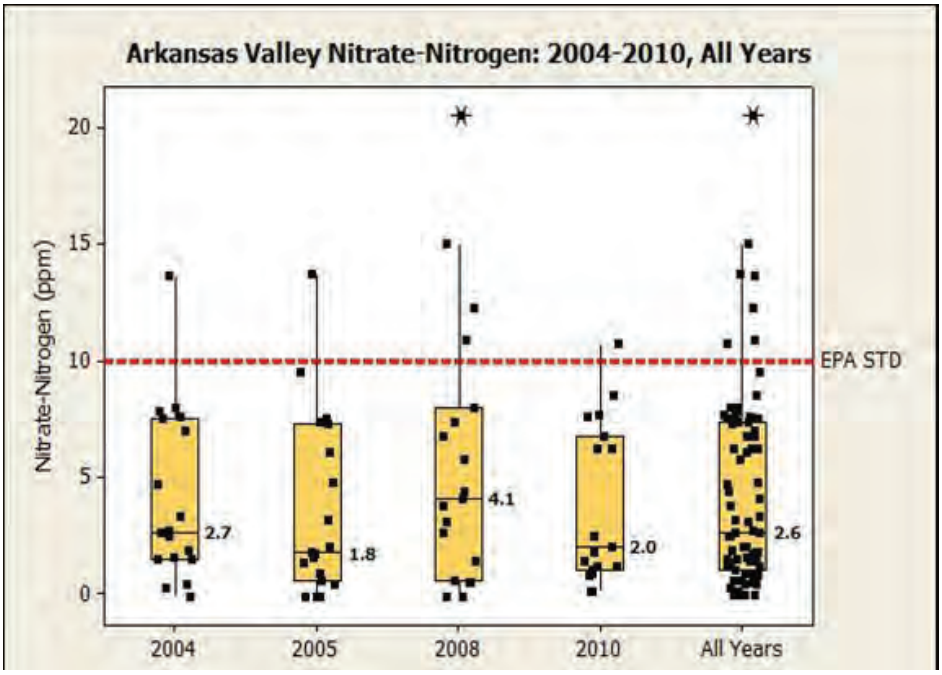

Figure 2. Box-whiskers plots of yearly nitrate-nitrogen results from Arkansas Valley monitoring wells and 'All Years' result since sampling of monitoring wells began in 2004. The boxed area contains 75% of the data. The median, or central tendency, is represented by the black horizontal line within the box. '*' represent values outside of the 99%. EPA STD is the nitrate-nitrogen EPA drinking water maximum contaminant level standard of 10.0 ppm.

were similar with only single detections of ethoprop, metolachlor, and metalaxyl at concentrations less than 1.0 ppb. The most consistently detected pesticide has been metolachlor which has been detected in only one well at concentrations of 0.58, 0.059, and 0.42 ppb in 2004, 2005, and 2008, respectively. **Figure 1** shows the configuration of the Arkansas Valley monitoring well network at the start of the 2010 sampling season. The damaged well discovered in 2008 was removed from the network since the new land–owner was not interested in allowing reinstallation.

2010 Sampling and Lab Analysis Notes

The Program conducted sampling of the network from September 7–17, 2010. All 19 wells were sampled as planned with samples being sent to two different locations: the Program's laboratory for analysis of pesticide compounds, nitrate and nitrite and to University of Colorado's Center for Environmental Mass Spectrometry (CEMS) for qualitative screening against a spectral database of more than 600 pesticide compounds. The purpose behind sending samples to the CEMS laboratory is to confirm the Program's current pesticide analytical approach, and to provide insight on potential compounds that are not currently being quantitatively analyzed by the Program, but may be reaching groundwater. Due to cost, a limited number of samples can be sent to the CEMS laboratory, and only four samples from the Arkansas Valley were delivered in 2010. Table 2 at the end of this report provides reporting limits for all quantitatively determined analytes in 2010. Detailed information on the Program's methods of detection for the various analytes tested for can be found on the Program's webpage.

2010 Nitrate Results

Nitrate–nitrogen results for samples collected in 2010 show only one well over the EPA standard and 11 other wells with less than five ppm. **Figure 2** demonstrates that nitrate concentrations discovered in this monitoring well network have usually been low compared to past sampling. The median nitrate for 2010 was half of what was reported in 2008, and the range of concentrations is similar to previous years. The all–time median of 2.6 ppm demonstrates that nitrate contamination in alluvial groundwater of the Arkansas River Valley is less of a concern than in other parts of Colorado where median concentrations have been found to be 10X higher.

One response that was first noticed in 2008, and found again in 2010, is the collection of wells, on the east end of the network between Lamar and Holly, in which nitrate–nitrogen ranges from 5–9.9 ppm. Along with the wells between Fowler and La Junta (**Figure 3**), these areas of slightly elevated nitrate are similar to what was discovered going back to 1994 and 1995. These are the areas of the Arkansas Valley alluvial aquifer that are likely the most prone to nitrate contamination due to hydrogeology and surface activities, and are continuing to exhibit those traits.

2010 Pesticide Results

There were a total of 12 detections of eight different pesticide compounds ranging in concentration from 0.11 to 1.21 ppb as can be seen in **Table 1**. Nearly 60% of those were of degradation products and 50% involved metolachlor constituents. **Figure 4** shows the distribution of detections in the nine wells having one or two pesticide compounds detected. The four samples sent to CEMS for qualitative analysis did not reveal any detection of pesticides not already being quantitatively determined by the Program's laboratory and actually only revealed presence of atrazine or its degradation products.

Part of the reason for an increase in total detections in 2010 was the implementation of a larger list of constituents being screened compared to 2008. The addition of the degradation products hydroxyl–atrazine and metolachlor–ESA accounted for half of the detections. The discovery of metolachlor and metolachlor–ESA in

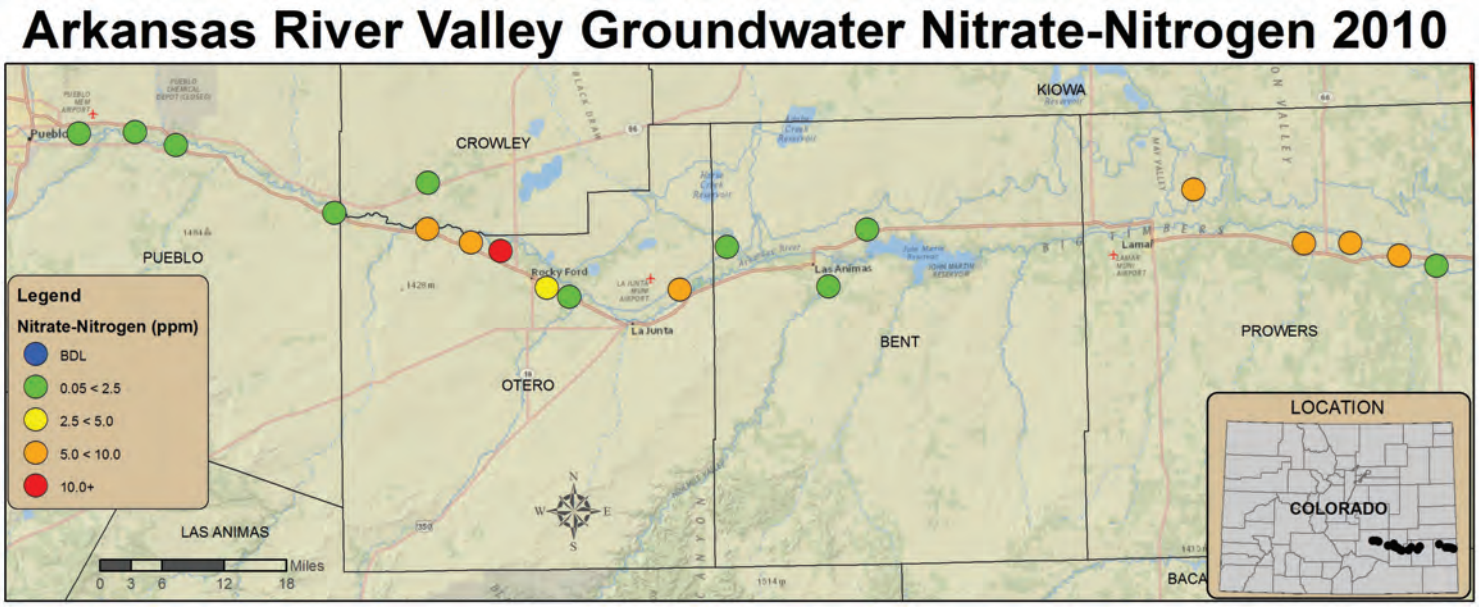

Figure 3. Distribution of 2010 nitrate-nitrogen concentrations in the Arkansas Valley network. A red symbol indicates a nitrate-nitrogen concentration at or above the EPA drinking water maximum contaminant level of 10.0 ppm.

the well on the east side of the network is in the same well that has had metolachlor detections in all previous years. The higher concentration of metolachlor ESA in this well shows that degradation has taken place but not enough for the entire parent compound to be consumed prior to leaching through to groundwater. This well's static water level is only 9.7 ft below ground surface so there is little residence time of metolachlor in the soil environment because of the shallow depth to water. The next well east (yellow symbol in Figure 4) had a detection of metolachlor–ESA at 0.85 ppb which was less than the 1.21 ppb detected in the well 4.5 miles due west suggesting this product is commonly used in the area and very low amounts of the active ingredient are reaching groundwater.

While a few other pesticide compounds were discovered for the first time, like imazethapyr and imazamox, the detection of 2,4–D is most surprising given how rarely it is detected in groundwater in Colorado despite it being widely used. While the concentration of 0.15 ppb is very low, the fact that it was detected at all at this site is unsual. The static water level at this site is 13.9 ft below ground surface, which suggests that at label prescribed application rates, the residence time achieved in nearly 10+ ft of soil should allow for full degradation given 2,4–D's typical soil half–life of ten days. More in–depth evaluation of land–use activities around this well will be conducted during the 2012 sampling season.

Summary

Figure 4. Distribution of 2010 pesticide detections in the Arkansas Valley network.

Arkansas Valley 2010 Pesticide Detections					
Pesticide	**# Detects**	**Minimum**	**Median**	**Mean**	**Maximum**
2,4-D	1	0.15			0.15
Desethyl atrazine*	1	0.42			0.42
Hydroxy atrazine*	1	0.11			0.11
Imazamox	1	0.17			0.17
Imazethapyr	1	0.23			0.23
Metalaxyl	1	0.59			0.59
Metolachlor	1	0.54			0.54
Metolachlor ESA*	5	0.47	0.71	0.74	1.21

Table 1. Pesticides detected in Arkansas Valley monitoring well samples in 2010. Concentrations are parts-per-billion (ppb). The EPA has established a primary drinking water maximum contaminant level of 70 ppb for 2,4-D, and a Lifetime Health Advisory Level for metolachlor of 70 ppb. '*' indicates a pesticide degradation product..

Consistent with historical findings, nitrate contamination in excess of the EPA standard of 10.0 ppm was not commonly discovered in the Arkansas Valley monitoring well network in 2010. The areas discovered to contain elevated concentrations of nitrate above a natural background of 2.5 ppm in 1994 and 1995 sampling, and relied on for delineation of the monitoring well network installed in 2004, continue to provide evidence of limited impacts to groundwater quality. However, the number of wells with nitrate above the EPA standard has continued to be very low and total nitrate impact in the monitoring well network is some of the lowest in the state.

Pesticide results for 2010 resulted in the largest number of detections to date partly because of changes in laboratory methodology since the last sampling in 2008, which added more than 50 new pesticide compounds to the analysis methodology. One new analyte, the metolachlor degradation product metolachlor–ESA, accounted for nearly half of the pesticide detections found in the network. Metolachlor has been detected in one particular well toward the eastern end of the network every year. The Arkansas Valley has not seen a pesticide concentration in excess of an EPA standard since the 1995 atrazine detection of 4.2 ppb. It is important to note however that not all compounds have EPA standards. In general, the low number of pesticide detections in 2010, show that groundwater pesticide contamination is not a common occurrence in the Arkansas Valley.

For questions or comments on this report, or the Program in general, please contact Rob Wawrzynski (303-239-5704, rob.wawrzynski@ag.state.co.us) or Karl Mauch (303-239-5713, karl.mauch@ag.state.co.us).

Table 2. Reporting limits of analytes tested for in 2010 by the Biochemistry Laboratory of the Colorado Department of Agriculture. Concentrations are in micrograms per liter (μg L^{-1}) for fungicide, herbicide, nematicide and insecticide analyte types. Concentrations for inorganic analytes are in milligrams per liter (mg L^{-1}).

Reporting Limits for Analytes Tested - Sampling Year 2010

Analyte	Tradename[1]	Use	Reporting Limit	Analyte	Tradename	Use	Reporting Limit
Nitrate as nitrogen (mg L^{-1})			0.05	3-Hydroxy carbofuran	Metabolite	Insecticide	0.25
Nitrite as nitrogen (mg L^{-1})			0.05	Halofenozide	Mach 2	Insecticide	0.10
Acetochlor	Harness	Herbicide	0.20	Halosulfuron methyl	Permit	Herbicide	0.10
Acetochlor (ESA)	Metabolite[2]	Herbicide	0.10	Hexazinone	Velpar	Herbicide	0.20
Acetochlor (OA)	Metabolite	Herbicide	0.25	Hydroxy Atrazine	Metabolite	Herbicide	0.10
Acifluorfen	Storm	Herbicide	0.10	Imazamethabenz methyl ester	Assert	Herbicide	0.10
Alachlor	Lasso	Herbicide	0.20	Imazamox	Raptor	Herbicide	0.10
Alachlor (ESA)	Metabolite	Herbicide	0.10	Imazapic	Plateau	Herbicide	0.10
Alachlor(OA)	Metabolite	Herbicide	0.10	Imazapyr	Arsenal	Herbicide	0.10
Aldicarb	Temik	Insecticide	0.50	Imazethapyr	Pursuit	Herbicide	0.10
Aldicarb sulfone	Metabolite	Insecticide	0.25	Imidacloprid	Admire	Insecticide	0.25
Aldicarb sulfoxide	Metabolite	Insecticide	0.10	Isoxaflutole	Balance	Herbicide	0.10
Aminopyralid	Milestone	Herbicide	0.50	Kresoxim methyl	Cygnus	Fungicide	0.25
Atrazine	Aatrex	Herbicide	0.10	Lindane	Gammexane	Insecticide	0.20
Azoxystrobin	Amistar	Fungicide	0.10	Linuron	Afalon	Herbicide	0.20
Bentazon	Basagran	Herbicide	0.50	Malathion	Malathion	Insecticide	0.20
Bromacil	Hyvar X	Herbicide	0.10	MCPA	MCPA	Herbicide	0.10
Carbofuran	Furadan	Insecticide	0.20	MCPP	Kilprop	Herbicide	0.10
Chlorantraniliprole	Durivo	Insecticide	0.10	Metalaxyl	Allegiance	Fungicide	0.20
Chlorimuron ethyl	Classic	Herbicide	0.25	Metconazole	Caramba	Fungicide	0.10
Chlorothalonil	Bravo	Fungicide	0.20	Methomyl	Lannate	Insecticide	0.10
Chlorsulfuron	Glean	Herbicide	0.10	Metolachlor	Bicep	Herbicide	0.20
Clopyralid	Lontrel	Herbicide	0.50	Metolachlor (ESA)	Metabolite	Herbicide	0.25
Cyanazine	Bladex	Herbicide	0.20	Metolachlor (OA)	Metabolite	Herbicide	0.25
Cyproconazole	Alto	Fungicide	0.10	Metribuzin	Lexone	Herbicide	0.20
Cyromazine	Larvadex	Insecticide	0.25	Metsulfuron methyl ester	Ally	Herbicide	0.10
2,4-D	Weed B Gone	Herbicide	0.10	Nicosulfuron	Accent	Herbicide	0.10
2,4-DB	Butyrac	Herbicide	0.50	Norflurazon	Solicam	Herbicide	0.20
DCPA	Dacthal	Herbicide	0.20	Picloram	Tordon K	Herbicide	0.50
Deethyl atrazine	Metabolite	Herbicide	0.10	Prometon	Pramitol	Herbicide	0.20
Deisopropyl atrazine	Metabolite	Herbicide	0.25	Propazine	Milo-Pro	Herbicide	0.20
Dicamba	Banvel D	Herbicide	0.50	Propoxur	Baygon	Insecticide	0.10
Dichlobenil	Casoron	Herbicide	0.20	Prosulfuron	Peak	Herbicide	0.25
Dichlorprop	Patron	Herbicide	0.10	Pyrimethanil	Distinguish	Fungicide	0.10
Diflufenzopyr	Distinct	Herbicide	0.10	Quinclorac	Drive	Herbicide	0.10
Dimethenamid	Frontier	Herbicide	0.10	Simazine	Primatol S	Herbicide	0.20
Dimethenamid (ESA)	Metabolite	Herbicide	0.25	Sulfentrazone	Spartan	Herbicide	0.50
Dimethenamid (OA)	Metabolite	Herbicide	0.50	Sulfometuron methyl ester	Oust	Herbicide	0.10
Dimethoate	Cygon	Insecticide	0.10	Sulfosulfuron	Certainty	Herbicide	0.10
Dinotefuran	Safari	Insecticide	0.20	Tebuconazole	Elite	Fungicide	0.10
disulfoton	Disyston	Insecticide	0.20	Tebufenozide	Confirm	Insecticide	0.10
disulfoton sulfone	Metabolite	Insecticide	0.20	Tebuthiuron	Graslan	Herbicide	0.10
disulfoton sulfoxide	Metabolite	Insecticide	0.20	Thiamethoxam	Cruiser	Insecticide	0.25
Diuron	Karmex	Herbicide	0.25	Triadimefon	Amiral	Fungicide	0.10
Ethofumesate	Solera	Herbicide	0.25	Triallate	Avadex BW	Herbicide	0.25
Ethoprop	Mocap	Insecticide	0.20	Triasulfuron	Amber	Herbicide	0.10
Fenamiphos	Nemacur	Nematicide	0.20	Trichlorfon	Dylox	Insecticide	0.20
Fenamiphos sulfone	Metabolite	Nematicide	0.20	Triclopyr	Garlon	Herbicide	0.50
Flufenacet	Axiom	Herbicide	0.10	Triticonazole	Charter	Fungicide	0.10
Flumetsulam	Broadstrike	Herbicide	0.10	Vinclozolin	Curalan	Fungicide	0.20

1 - Tradenames used are strictly examples of products containing a particular analyte and does not suggest analysis of a specific product.
2 - 'Metabolite' is a degradation product of a parent pesticide.